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APPLICATION NUMBER: ***60/510,201***
FILING DATE: ***October 10, 2003***
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Certified by

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Attorney's Docket No. JJD-0311 *"PATENT"*

Family Number P2003J083

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

03917 U.S. PTO
60/510201
101003

In re application of: Ramesh Varadaraj et al

For: ENHANCING ATOMIZATION OF FLUIDS

Commissioner for Patents
Mail Stop: Provisional Patent Application
P.O. Box 1450
Alexandria, Virginia 22313-1450

COVER SHEET FOR FILING PROVISIONAL APPLICATION (37 C.F.R. § 1.53(c))

CERTIFICATION UNDER 37 C.F.R. 1.10 *
(Express Mail label number is mandatory) ***(Express Mail certification is optional)***

[X] "Express Mail" mailing label number EU862908676US. Date of Deposit OCTOBER 10, 2003.
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Phyllis A. Taylor
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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.53(c):

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):
2. The name(s) of the inventor(s) is/are:

	GIVEN NAME	MIDDLE INITIAL OR NAME	FAMILY (OR LAST) NAME
1.	Ramesh	--	Varadaraj
2.	Stuart	Scott	Goldstein
3.	George	Alexander	Swan III
4.	William	Russell	Adamson

27810
PATENT TRADEMARK OFFICE

Attorney's Docket No. JJD-0311 Family Number: P2003J083

3. Residence address(es) of the inventor(s), as numbered above:

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   3. 18437 Wildlife Way, Baton Rouge, Louisiana 70817, USA
   4. 2510 Gates Circle #21, Baton Rouge, Louisiana 70809, USA

4. The title of the invention is:

   ENHANCING ATOMIZATION OF FLUIDS

5. The name, registration, customer and telephone numbers of the attorney is:

Name of Attorney(s):	Paul E. Purwin	/ Erika S. Wilson	/ Gerald J. Hughes
Registration Number(s):	29,203	/ 52,368	/ 41,855
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Customer Number 27810 Deposit Account No. 05-1330

6. The docket number used to identify this application is: Docket No. JJD-0311

7. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government;

   This invention was made by an agency of the United States Government, or under contract with an agency of the United States Government.

   [X] No.

   [ ] Yes.

   The name of the U.S. Government agency and the Government contract number are: ______

8. Identification of documents accompanying this cover sheet:

   A. Documents required by 37 C.F.R. §§ 1.51(c)(2)-(3):

   [X] Specification Number of pages: 15

   [X] Drawings Number of sheets: 3

   B. Additional documents:

   [X] Claims Number of claims: 11

   [ ] Assignment

   [ ] Other: ______

The PTO did not receive the fo[illegible] listed item(s) specif° = 12 only
Claims 3 only

Attorney's Docket No. JJD-0311 Family Number: P2003J083

9. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is $ 160.00 for other than a small entity.

10. Method of fee payment

[X] Charge Deposit Account No. 05-1330 in the amount of $ 160.00.
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Date: October 9, 2003

Paul E. Purwin
Signature of Attorney

Address to which correspondence is to be sent:

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JJD:kak/jdw
10/9/03

APPLICATION FOR UNITED STATES PATENT

ENHANCING ATOMIZATION OF FLUIDS

Applicants: Ramesh Varadaraj
Stuart S. Goldstein
George A. Swan
W. Russell Adamson

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PHYLLIS A. TAYLOR
(Typed or printed name of person mailing paper or fee)

Phyllis A. Taylor
(Signature of person mailing paper or fee)

CASE NO. JJD-0311

27810
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ENHANCING ATOMIZATION OF FLUIDS

FIELD OF INVENTION

[0001] The present invention relates generally to the atomization of fluids. More particularly, the invention is concerned with enhancing the atomization of fluids, especially fluidized cat cracker (FCC) feeds by using chemical means in conjunction with atomization hardware.

BACKGROUND OF INVENTION

[0002] Atomizing a fluid by passing it through an orifice into a lower pressure zone to produce a spray of droplets is a technique used in a wide variety of applications and processes. For example, in fluidized catalytic cracking (FCC) processes relatively viscous petroleum feeds are converted into more valuable products including gasoline, jet fuel, and heating oil. In a FCC process, a preheated oil feed is mixed with steam and the resulting two phase fluid is passed into a lower pressure atomization zone in which the oil is atomized and brought into contact with a particulate, hot, cracking catalyst. The feed then is converted into lower boiling products.

[0003] The trend in FCC technology has been to use more active catalysts thereby reducing the length of time the feed needs to be in contact with the catalyst. To take advantage of a short contact time, however, the oil needs to be uniformly distributed in the form of small droplets. Indeed, experience has shown that long oil vaporization times lead to higher yields of undesirable, low value products. Additionally, as feeds become heavier the fraction of steam dispersion gas must be increased to facilitate atomization. Many FCC units, however, have limited steam capacity which constrains their ability to effectively process heavier feeds. Considerable effort therefore has been

devoted to try to find improved ways for atomizing the oil feed in FCC processes. Examples of such are found in, for example, U.S. Patent 5,289,976, U.S. Patent 5,173,175, U.S. Patent 6,093,310 and U.S. Patent 6,352,639 B2.

[0004] Despite the advances made in atomization hardware, and especially FCC feed injection hardware, it would be an improvement in the art if a way could be found to enhance oil atomization in conjunction with hardware and process constraints.

[0005] Thus, an object of the present invention is to enhance oil atomization in a FCC process.

[0006] Another object of the invention is to provide a narrow distribution of small droplets of a feed-in-steam dispersion when the dispersion mixture is passed through a nozzle into a FCC unit.

[0007] Other objects will become apparent from a reading of the description of the invention below.

SUMMARY OF INVENTION

[0008] Broadly stated, the atomization of a fluid injected into an atomization zone is enhanced by providing the fluid with an effective amount of an additive capable of reducing the static and dynamic interfacial tension between the components comprising the fluid.

[0009] In the context of a FCC process, the atomization of a hydrocarbon and steam mixture injected into the atomization zone of a FCC reactor is enhanced by providing the hydrocarbon and steam mixture with an effective amount of an additive capable of reducing the static and dynamic interfacial tension between the hydrocarbon and the steam wherein the additive is thermally stable at pre-

injection temperatures and which will decompose under the temperature and other conditions in the FCC reactor.

BRIEF DESCRIPTION OF DRAWINGS

[0010] Figure 1 is a plot showing the dynamic interfacial tension (denoted as dynamic IFT) of two different surfactants in water.

[0011] Figures 2 and 3 show plots of mean droplet diameter vs. steam weight % for oil and steam additized with a surfactant (squares) and oil and steam with no additive (diamonds).

DETAILED DESCRIPTION OF INVENTION

[0012] The present invention is applicable to a wide variety of process requiring atomization of feeds, especially where very small droplet sizes of the feed, e.g., below about 500 μ are desirable. For convenience, however, the invention will be described in connection with improving feed injection into a FCC process reactor.

[0013] In FCC processes a petroleum oil is preheated to a temperature typically in the range of about 125°C to 500°C, mixed with steam typically at a steam pressure of 100 to 600 psi and in an amount of 0.5 to 5 wt% based on the weight of oil to provide a mixture of oil and steam which then is passed through an atomizing nozzle into the FCC process reactor to provide droplets of oil-in-steam which contact a catalyst in the reactor resulting in conversion of the feed into lower boiling, more valuable products.

[0014] In the present invention the atomization of an oil and steam feed injected into the reactor via the nozzle is enhanced by providing the feed with an effective amount of an additive that is capable of reducing the static and

dynamic interfacial tension between the oil and steam. Reducing the interfacial tension results in a narrow distribution of small droplets. Small oil droplets size increases oil vaporization rate and effectiveness and provides better contacting of the oil and catalyst. For example, a 25% reduction in the mean oil droplet diameter boosts vaporization rate by 35% to 50%. Shorter vaporization times improve the yield of desirable products.

[0015] The additive added will be one which is thermally stable at temperatures to which the feed is preheated and which will decompose under conditions existing in the FCC reactor. Preferably, the additive will exclude components containing sulfur, nitrogen and metals. Suitable additives include non-ionic surfactants and mixtures thereof having hydrophilic lipophilic blanance values HLB's typically in the range of about 3 to about 20. Examples of such surfactants include alkyl alkoxylates, preferably alkyl ethoxylates and mixtures of aldehydes and ketones preferably alkyl aldehydes acids and ketones and more preferably alkyl aromatic aldehydes and ketones and acids.

[0016] In general the amount of surfactant or mixture of surfactants will be sufficient to reduce the static and dynamic interfacial tension of the oil and steam such that the atomized the oil drops will have a mean droplet diameter less than about 500 μ.

[0017] In one detailed FCC embodiment the invention comprises the steps of:

(a) providing a mixture comprising a surfactant or mixture of surfactants and steam;

(b) passing the mixture into a flowing, hot, liquid FCC feed oil to form a two-phase fluid; and

(c) passing the two-phase fluid through an atomizing means with an atomizing zone in the FCC reactor to form a dispersion comprising droplets of the oil feed wherein the oil drops have mean droplet diameter less than that achieved in the absence of the surfactant.

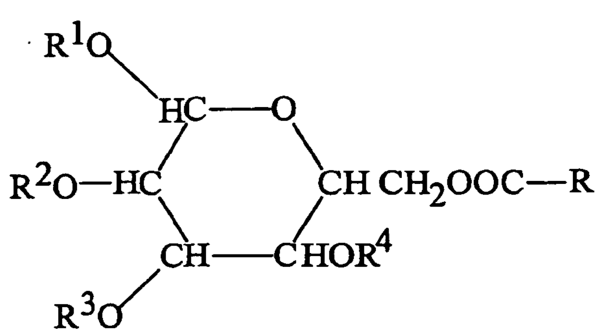
Indeed, the mean droplet diameter typically will be less than about 500 μ.

[0018] The mixture of surfactants or surfactants and steam may be prepared either by any one or a combination of adding the surfactant to steam or vaporizing the surfactant and introducing the vaporized surfactant into the steam or adding the surfactant to water and heating the surfactant solution to provide a steam and surfactant mixture.

[0019] In this embodiment alkyl alkoxylate type surfactants are particularly suitable at treat rates in the range of about 25 ppm to 50,000 ppm based on the weight of steam, and preferably in the range of 50 to 10,000 ppm. Especially preferred are alkyl ethoxylates are represented by formulae I to III:

$$RO(CH_2CH_2O)_nH \qquad \text{I}$$

$$R\text{—}CO(CH_2CH_2O)_nH \qquad \text{II}$$

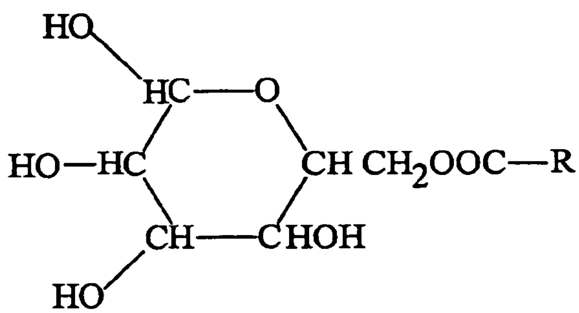


III

where R is a linear or branched alkyl group of 3 to 24 carbon atoms; n is from 1 to 10 and preferably from 1 to 5; R^1, R^2, R^3 and R^4 are independently

alkoxylate groups, $(R^5O)_mH$ where R^5 is an alkylene group of 2 to 4 carbon atoms and m is from 1 to 20 and preferably from 3 to 15.

[0020] When additive III is used, it is preferred to use it in combination with an alkyl sorbitan of structure IV.



IV

For the alkyl sorbitan it is preferred R is an alkyl group of 3 to 24 carbon atoms. When used in combination with III the ratio of additive III/IV is preferably between about 95/5 to 30/20 and more preferably about 80/20 to 30/70 and even more preferably 75/25 to 50/50.

[0021] In yet another detailed FCC embodiment the invention comprises the steps of:

(a) providing a mixture of a surfactant or mixture of surfactants and a hot, liquid FCC feed oil;

(b) passing steam into the mixture of step (a) to form a two-phase fluid; and

(c) passing the two-phase fluid through an atomizing means into an atomizing zone in a FCC reactor to form a dispersion comprising droplets of the oil feed wherein the oil drops have a mean droplet diameter less than that achieved in the absence of the surfactant and wherein, for example, the mean droplet diameter will be less than 500 μ.

[0022] Commercially available surfactants of the type I, II, III and IV mentioned earlier may be used. When the oil is provided with the surfactant or mixture of surfactants the amount of additive generally is in the range of 50 to 20,000 ppm based on the weight of oil and preferably in the range of 50 to 5,000 ppm. Alternatively, a petroleum oil containing alkyl substituted 1, 2 and 3 ring aromatic compounds may be oxidized to generate a suitable mixture of oxidized products suitable as additives for the invention. The oxidization is conducted by heating the oil from about 150°C to about 200°C, in the presence of air for a time sufficient, typically about 4 hours, to produce the oxidized products suitable as additives for the invention. Typically such oxidation produces aldehydes, ketones and acids.

[0023] In this embodiment it is preferred to take a slip stream of the FCC oil feed for the oxidation step and thereafter mix the oxidized stream with the FCC oil feed.

EXAMPLES

Example 1

[0024] Span 80, Tween-80, Brij-35, Brij-58 and Brij-700 surfactants were used to additize water. Span, Tween and Brij are trademarks of ICI Americas Inc. The chemical structure of the Brij, Tween and Span surfactants is the same as formula II, III and IV respectively as previously given.

[0025] The air/water equilibrium interfacial tension of a 0.1 wt% solution of the surfactants in water was determined for each surfactant by the Wilhelmy plate method at 25°C. The corresponding air/water equilibrium interfacial tensions are shown in Table 1. A substantial reduction in interfacial tension (from 72 dyne/cm for untreated water) was achieved.

TABLE 1

BRIJ	R	m	HLB	IFT (dyne/cm) (+/- 1)
35	C12	23	16.7	31
52	C16	20	15	42
700	C18	100	18.8	49
TWEEN				
80	C18	$R_1 + R_2 + R_3 + R_4 = -(CH_2\text{-}CH_2O)_{20}\text{-}H$	15	41
Span 80	C18			

Interface: Air/Water

[0026] The dynamic interfacial tension of Tween 80 in Brij 58 in water was determined by the differential bubble pressure method and the results are shown in Figure 1. Within two seconds the equilibrium interfacial tension is reached for both surfactants.

Example 2

[0027] Neodol 91-2, a surfactant which is a trademark of Shell Chemical Company was used to additize water. The chemical structures of the surfactant is shown below:

$$R\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_m\text{-}H$$

Neodol: R = linear C_9H_{19}, m = 2

[0028] The FCC feed oil/water interfacial tension at 2000 ppm treat rate of Neodol in water was determined by the pendant drop method at 176°F (80°C)) (Table 2). At least 70% reduction in interfacial tension was observed for the Neodol additive.

TABLE 2

Feed	IFT {+/-1} (dynes/cm)
FCC Feed Oil / Water	20
FCC Feed Oil / 1000 ppm Neodol 91-2 in water	6

Example 3

[0029] Two distilled water samples, one containing 1000 ppm of Neodol 91-2 and the other 1000 ppm of Exxal DDA-3 were prepared. Exxal DDA-3 is a trademark of ExxonMobil Chemicals with formula I where n = 3 and R is branched $C_{12}H_{25}$ group. The samples were heated to 212°F (100°C) with vigorous mixing to produce steam. Steam was collected and condensed in a receiving vessel. Surface tension was measured on the distilled water containing 1000 ppm surfactant and on the condensed water in the receiving vessel. Surface tension of water was 72 dynes/cm. Values of surface tension lower than 72 dynes/cm indicate the presence of surfactants in water. Identical surface tensions for the distilled water containing 2000 ppm surfactant and for the condensed water in the receiving vessel indicate that the surfactants vaporize with steam. The results are shown in Table 3.

TABLE 3

Feed	IFT {+/- 0.5} (dynes/cm)
Water	72
1000 ppm Neodol in water	25.6
Condensed water in receiving vessel	26.8
100 ppm Exxal DDA-3 in water	25.6
Condensed water in receiving vessel	27.6

Example 4

[0030] FCC feed atomization experiments were conducted to determine the influence of oil additization and steam additization on droplet size. In the case of oil additization, the oil was additized with a Tween 80/Span 80 mixture in the ratio of 60/40 at a treat rate of 2000 ppm based on the weight of oil. The oil with additive was preheated to 150°F (66°C). The preheated oil was passed through a calibrated rotameter at 3 g/sec, and further heated to 450°F (232°C). Superheated steam at 450°F (232°C) was produced using a flash vaporization heater. The water inlet to the flash vaporization heater was monitored using a rotameter.

[0031] The superheated steam and oil was mixed in a T-junction, and passed through a feed injector, 120 mm long and 1.4 mm in diameter. The pressure and temperature of the oil and steam mixture were monitored at the T-junction using a thermocouple and a pressure gauge. The oil and steam mixture was sprayed horizontally into an exhaust system, which separated the oil from the steam.

[0032] A Malvern particle diameter analyzer was positioned 3 inches from the exit of the feed injector. Drop sizes were obtained at each operating condition for three separate runs. Good repeatability between the runs was observed. The flow rate was maintained within +/- 2% during the duration of data collection. The temperature was also maintained within +/- 2°C during the same period. Figure 2 shows the results, namely a reduction in droplet size.

[0033] In the case of steam additization, Neodal 91-2 was added to water at a treat rate to produce 2000 ppm of Neodol based on the weight of steam, the water heated to produce a mixture of steam and additive and the mixture was then mixed with the oil in a T-junction. Thereafter the procedure as with oil additization was followed.

[0034] The effect of the Neodol steam additive on the Sauter Mean Diameter (SMD) (SMD = diameter of liquid oil droplet with the same volume/surface ratio as the entire spray) of drop sizes is shown in Figure 3. A 5-10% reduction in oil droplet SMD was obtained with Neodal additization of steam.

Example 5

[0035] 200 g of a crude oil from western Canada was placed in a three-necked glass flask and heated to a temperature of 150°C to 180°C for 4 hours with a continuous purge of air at 80 to 100 scf/bbl/hour. After completion of reaction the product was tapped hot from the reactor. The product was added to n-decane at various concentrations and mixed. Equilibrium oil/water interfacial tension was determined using the pendant drop described in the art. Results are shown in Table 4.

TABLE 4

Wt% AO Product	Interfacial Tension dynes/cm
None	56
0.1	22
1	25
10	30

[0036] For all concentrations of product added to n-decane, a substantial decrease in interfacial tension was observed, which is forecast to correspondingly improve atomization of the liquid hydrocarbon.

WHAT IS CLAIMED IS:

1. A method of enhancing the atomization of a fluid mixture injected into an atomization zone comprising providing the fluid mixture with a sufficient amount of an additive capable of reducing the static and dynamic interfacial tension of the components of the mixture, such that when atomized the fluid mixture will form drops having a mean droplet diameter less than that achieved in the absence of the additive.

2. The method of claim 1 wherein the additive is selected from surfactants and mixtures of surfactants having a HLB in the range of about 3 to about 20.

3. In the atomization of a preheated hydrocarbon-steam feed into the atomization zone of a FCC reactor, the improvement comprising providing the feed with an additive capable of reducing the static and dynamic interfacial tension of the hydrocarbon and steam the additive being thermally stable at the preheated temperatures and which will decompose under conditions in the FCC reactor, the additive being present in an amount sufficient such that when atomized the hydrocarbon and steam will form drops having a mean droplet diameter less than that achieved in the absence of the additive.

4. The improvement of claim 3 wherein the additive is selected from surfactants and mixtures of surfactants having a HLB in the range of about 3 to about 20.

5. The improvement of claim 4 wherein the additive is added to water, the water converted to steam and the steam mixed with a hot, liquid oil feed.

6. The improvement of claim 4 wherein the additive is vaporized and added to steam which then is mixed with a hot, liquid oil feed.

7. The improvement of claim 4 wherein the additive is added to the preheated hydrocarbon and steam.

8. The improvement of claim 3 wherein the additive is formed by heating a petroleum hydrocarbon at a temperature in the range of about 150°C to about 200°C and aerating the heated hydrocarbon for a time sufficient to form a mixture of additive in the hydrocarbon.

9. The improvement of claim 8 wherein the mixture of additives in the hydrocarbon is added to a hot, liquid oil feed to which then is added steam to provide the feed with the additives.

10. A FCC process comprising:

(a) providing a preheated hydrocarbon-steam feed with an additive selected from nonionic surfactants and mixtures thereof having a HLB in the range of about 3 to about 20 and which additive is thermally stable at the temperature to which the feed is preheated;

(b) passing the feed provided with additive through an atomizing zone in a FCC reactor to form droplets;

(c) contacting the droplets in the FCC reactor with cat cracking catalyst whereby the feed is converted to lower boiling products; and

wherein the amount of additives provided is sufficient such that the droplets formed have a mean particle diameter less than that achieved in the absence of the additive.

11. The process of claim 10 wherein the feed is provided with the additive by adding the additive to one of water, steam or hydrocarbon before forming the hydrocarbon steam feed or adding the additive to the feed.

ENHANCING ATOMIZATION OF FLUIDS

Abstract of the Disclosure

The atomization of a fluid injected into an atomization zone is enhanced by providing the fluid with an effective amount of an additive capable of reducing the static and dynamic interfacial tension of the fluid components whereby the fluid will form drops having a mean diameter less than that achieved in the absence of the additive.

FIGURE 1

Dynamic Interfacial Tension of Tween 80 (circles) and Brij 58 (diamonds)

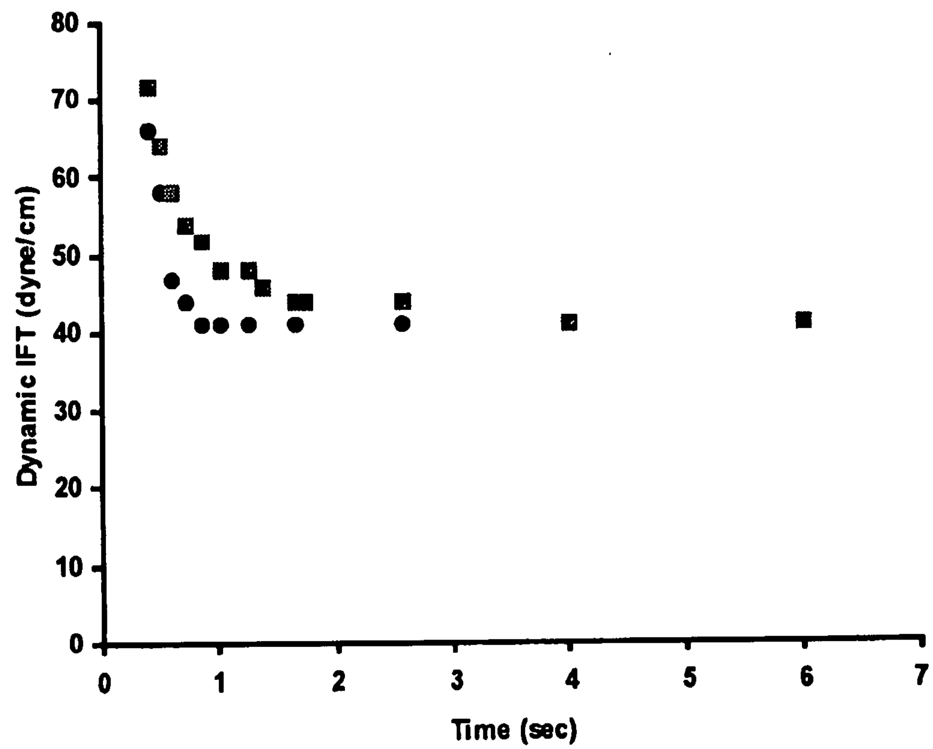
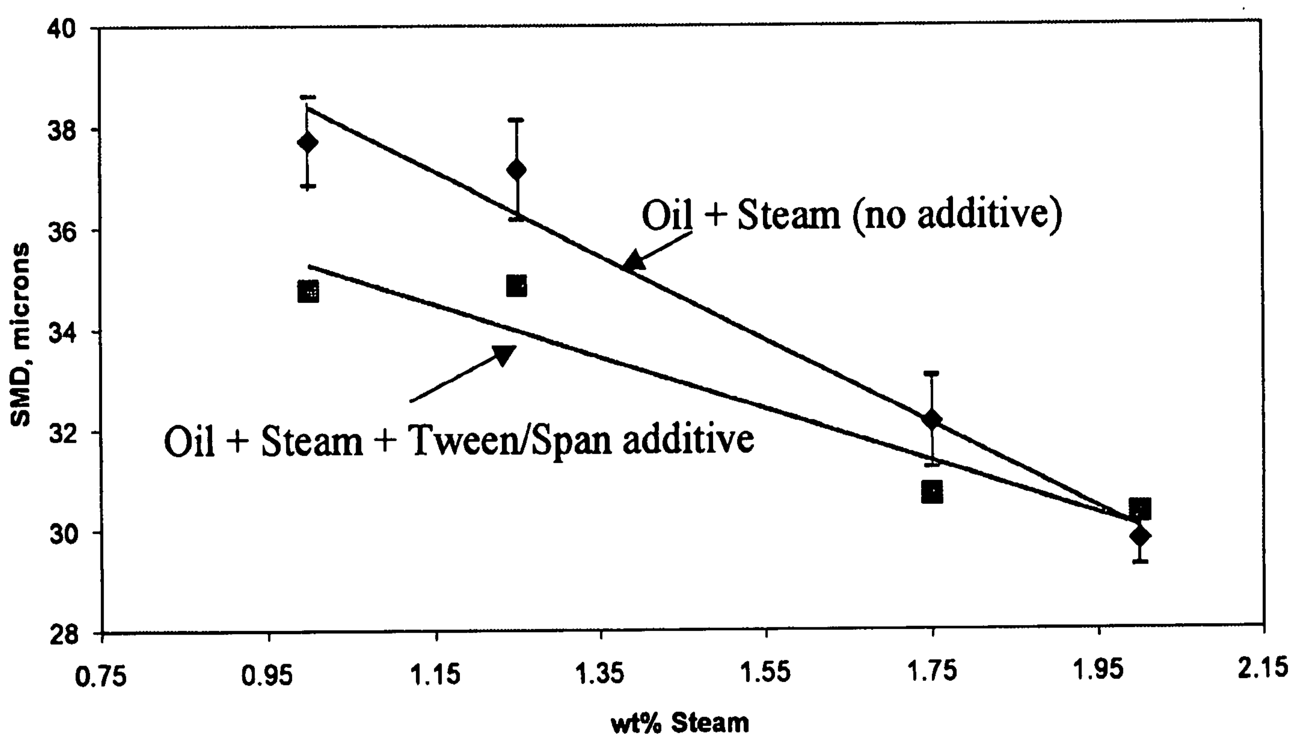


FIGURE 2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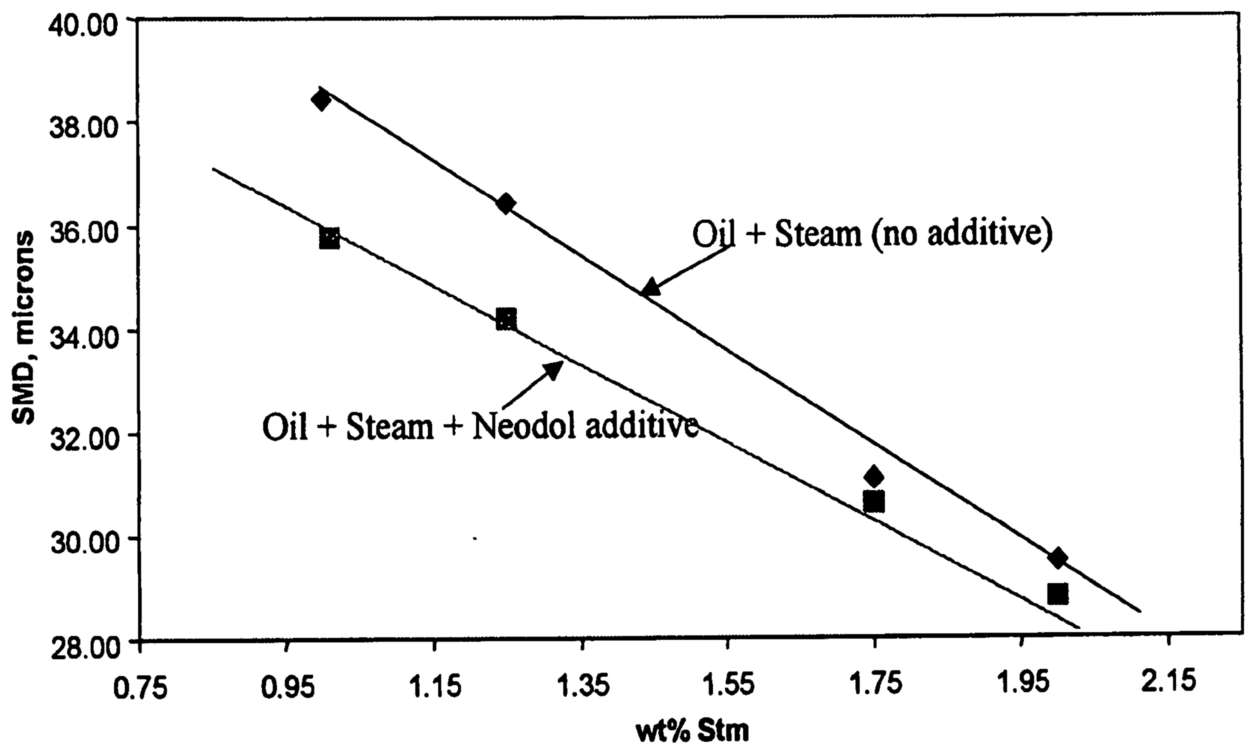
Oil + Steam + Tween/Span additive

FIGURE 3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wt% Stm
Oil + Steam (no additive)
Oil + Steam + Neodol additive

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